

KFM 23: Focus Session: Fermi level engineering of functional ceramics

We will discuss the role of the Fermi level as key quantity for predicting and controlling properties of functional ceramics. The focus will be on doping and compensation effects in functional ceramics, including i.e. fuel cells, batteries, membranes, piezoceramics and electroceramics. Experimental and theoretical contributions, which focus on the interplay of compensation effects by electrons, holes, polarons and ions, as well as the role of grain boundaries, surfaces and heterogeneous interfaces are invited to contribute to this special symposium.

Chair: Karsten Albe (TU Darmstadt)

Time: Thursday 9:30–11:50

Location: E 124

Invited Talk KFM 23.1 Thu 9:30 E 124
The Research Center FLAIR: Fermi Level Engineering of Oxide Electroceramics — ●ANDREAS KLEIN — Technical University of Darmstadt, Institute of Materials Science

Chemical substitution is the primary strategy to tailor material properties. Isovalent substitution changes the density of states while heterovalent substitution, i.e. doping, can induce electronic compensation, ionic compensation, valence changes of cations or anions, or result in the segregation or neutralization of the dopant. While all these can, in principle, occur simultaneously, it is often desirable to select a certain mechanism in order to determine material properties. Being able to predict and control the individual compensation mechanism should therefore be a key target of materials science. This contribution outlines the perspective that this could be achieved by taking the Fermi energy as a common descriptor for the different compensation mechanisms. This generalization becomes possible since the formation enthalpies of the defects involved in the various compensation mechanisms do all depend on the Fermi energy. In order to control material properties, it is then necessary to adjust the formation enthalpies and charge transition levels of the involved defects. Understanding how these depend on material composition will open up a new path for the design of materials by Fermi level engineering. This is the target of the research center FLAIR (www.mawi.tu-darmstadt.de/flair), which has been established in January 2023 by the German Research Foundation. The scientific concept of the center is published in [1]. [1] A. Klein et al., *J. Electroceramics*, doi: 10.1007/s10832-023-00324-y

KFM 23.2 Thu 10:00 E 124
Operando XPS Study with electrochemical cell setup — ●SAVITA CHAUDHARY, PENGCHENG HU, BINXIANG HUANG, KIM ALEXANDER CREUTZ, YUE LIU, GERO JOHANNES PICKEL, VINIT AGARWALLA, ALEXANDER FREBEL, and ANDREAS KLEIN — Technical University of Darmstadt, Darmstadt, Germany

The change of the oxygen content in a material using an electrochemical cell is an important asset to understand the variation of the Fermi energy in materials, paving the way for Fermi level engineering as a versatile toolkit for designing a broad range of materials according to specific applications. The electrochemical cell is constructed by top and bottom electrodes deposited on an oxygen ion conducting electrolyte. The reduction or increase of the oxygen content in the electrodes by cathodic or anodic polarization, is accompanied by an increase or lowering of the Fermi energy, respectively. The latter can be monitored together with chemical changes of the sample if the electrochemical cell is operated in an X-ray photoelectron spectrometer. We will present experiments using Y-stabilized zirconia, Fe-doped SrTiO₃, (1-x)Pb(Mg_{1/3}Nb_{2/3})O_{3-x}PbTiO₃(PMN-PT), Na_{1/2}Bi_{1/2}TiO₃-BaTiO₃ (NBT-BT) or (Pb,La)(Zr,Sn,Ti)O₃ (PLZST) as electrolytes, and (Sn-doped) In₂O₃, SrFeO_{3-δ} and Sr-doped LaCoO_{3-δ} as electrode materials. The use of the setup to quantify the Fermi energies of charge transition levels in either the electrolyte or the electrode will be demonstrated.

KFM 23.3 Thu 10:20 E 124
Machine Learning Potential for BaTiO₃ — ●AMIT SEHRAWAT — Materials Modelling Division, Otto-Berndt-Str. 3 64206 Darmstadt

Barium titanate (BaTiO₃, BTO), a well-known perovskite oxide, undergoes intricate ferroelectric phase transitions. These transitions are characterized by a shift from a paraelectric cubic phase at high temperatures to a sequence of low-temperature phases (Cubic → Tetragonal → Orthorhombic → Rhombohedral), predominantly driven by anti-ferrodistortive modes. Although *ab-initio* molecular dynamics is used to explore the finite-temperature properties, the high computational

cost and scaling to only a few hundred atoms restricts the study for a longer time and length scale. Conversely, classical molecular dynamics simulations, though efficient in understanding atomic-scale dynamics, often lack accuracy compared to first-principles-based methods. To overcome these limitations, we develop a machine learning interatomic potential (MLIP) for BaTiO₃, based on Atomic Cluster Expansion (ACE) formalism using data from density functional theory (DFT) calculations. The ML potential achieves DFT-level accuracy while facilitating simulations over significantly longer time and length scales. Using trained potential, our research investigates the temperature-driven cubic-to-Rhombohedral phase transition in BTO and examines the influence of pressure on the transition temperature.

KFM 23.4 Thu 10:40 E 124
Fermi-level Engineering of Ba-rich perovskite oxide materials by introducing fluorine — ●SYLVIA LORRAINE KUNZ, LAXMIPRIYA SAHOO, and OLIVER CLEMENS — Institute for Materials Science, University of Stuttgart, 70569 Stuttgart, Germany

Perovskite compounds ABO₃ are renowned for their structural and compositional flexibility. They exhibit variations on both the cation A and B sites, as well as on the anion sublattice [1]. The introduction of anions in the host lattice has an impact on the coordination sphere of the cations, influencing their oxidation states and consequently affecting the Fermi energy [2]. By investigating the substitutional effects, a Fermi-level guided synthesis approach could be derived to tailor specific electronic properties.

In this contribution, we systematically exemplify the relationship between the Fermi energy and sample synthesis in the context of the topochemical fluorination of Ba-rich transition metal oxides BaFe_{1-x}Co_xO_{3-d}F_y, BaFe_{1-x}Ti_xO_{3-d}F_y, BaCo_{1-x}Ti_xO_{3-d}F_y with varying amount of fluorine (0 ≤ y ≤ 1). The fluorination of Ba-rich transition metal oxides was achieved through a topochemical reaction route at 370 °C, utilizing PVDF as fluorination agent [3]. We will discuss the potential impact on structural and compositional changes on the Fermi-Level of these compounds.

References [1] Kobayashi, Y.; Tsujimoto, Y.; Kageyama, H.. *Annu. Rev. Mater. Res.* 2018, 48, 303-326. [2] Clemens, O.; Slater, P. *Rev. Inorg. Chem.* 2018, 33 (2-3), 105-117. [3] Perween et al, *Inorg. Chem.* 2023, 62, 40, 16329-16342.

KFM 23.5 Thu 11:00 E 124
fermi-level involved phase field modeling of grain growth in the perovskite oxide SrTiO₃ — KAI WANG and ●BAIXIANG XU — Mechanics of Functional Materials (MFM), TU-Darmstadt, Darmstadt, Germany

The grain boundary (GB) distribution and the interaction between GB with point defects in polycrystalline ceramics significantly determine the macro properties of the materials. In order to investigate the GB properties, we developed an electro-chemo phase field model to reproduce space charge effects and the distribution of different point defects in bulk and along GB. The performance of this phase field model is benchmarked with sharp interface calculations by simulating the Fe-doped perovskite oxide SrTiO₃ (STO) at the equilibrium state when iron defects in STO are immobile and mobile. Moreover, through considering the influence of fermi-level, different dopants with various valencies are taken into account in the phase field simulations. Then, the corresponding space charge effects are studied.

Invited Talk KFM 23.6 Thu 11:20 E 124
Designing Transition Metal Oxynitrides for Photoelectrochemical Applications — ●VERENA STREIBEL^{1,2}, LAURA I. WAGNER^{1,2}, JOHANNA L. SCHÖNECKER^{1,2}, ELISE SIROTTI^{1,2}, JOHANNA EICHHORN^{1,2}, SASWATI SANTRA^{1,2}, and IAN D. SHARP^{1,2}

— ¹Walter Schottky Institut, TU München, Garching, Germany —
²Physics Department, TUM School of Natural Sciences, TU München,
Garching, Germany

Transition metal oxynitrides are an emerging class of functional materials with tunable electronic and optical properties. They offer a high potential for tailored materials development since their Fermi levels, energy band gaps, valence/conduction band positions, and surface chemistry can be controlled by adjusting the cation and anion composition. These design opportunities are especially important for photoelectrochemical applications. Here, we discuss our approach to

developing transition metal oxynitride thin films as photoelectrodes using reactive sputter deposition. First, we focus on the influence of the anion ratio in the zirconium oxynitride system. At sufficiently high oxygen concentrations, we observe the opening of a band gap in the UV-visible range and the emergence of photoelectrochemical activity for oxidation reactions. Second, we focus on cation substitution in the titanium tantalum (oxy)nitride system.[1] We demonstrate that controlled Ti-doping of Ta₃N₅ thin films dramatically reduces the concentration of deep-level defects and thereby enhances the photoelectrochemical activity.

[1] Wagner, Streibel, Sharp, et al., *Adv. Func. Mat.*, 2023, 2306539.